Inorganica Chimica Acta, 221 (1994) 9–15

The steric effect on the ring opening process of the decarboxylation of *cis*-carbonato-bis(diamine)cobalt(III) ions

Salah S. Massoud[*,†]
Department of Chemistry, Faculty of Science, Alexandria University, PO Box 426, Ibrahimia, Alexandria 21321 (Egypt)

R.B. Jordan
Department of Chemistry, University of Alberta, Edmonton, Alta., T6G 2G2 (Canada)

(Received July 2, 1993; revised September 6, 1993)

Abstract

The aquation of carbonatotetraaminecobalt(III) ions; $[Co(N_2)_2CO_3]^+$ where (N_2) is 1,1,2,2-tetramethylethylenediamine (tme) and *N,N'*-dimethylethylenediamine (bmen) has been studied in aqueous 1.0 M $HClO_4/NaClO_4$. For tme, the $HClO_4$ is 0.01–0.20 M and the temperature is 20, 25, 30 and 35 °C; for bmen, the $HClO_4$ is 0.15–0.55 M and the temperature is 55 and 63 °C. Both complexes hydrolyse to form the *cis*-diaqua product, and the rate law is $d(\ln[\text{complex}])/dt = k_0 + k_1[H_3O^+]$. The values of the rate constant (25 °C), $\Delta H^{\ddagger}$ (kcal mol^{-1}) and $\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1}) are: for $[Co(tme)_2CO_3]^+$, $k_0 = 2.59 \times 10^{-4}$ s^{-1}, $\Delta H_0^{\ddagger} = 18.6 \pm 1.8$, $\Delta S_0^{\ddagger} = -12.6 \pm 8.5$; $k_1 = 2.86 \times 10^{-2}$ M^{-1} s^{-1}, $\Delta H_1^{\ddagger} = 11.4 \pm 1.0$, $\Delta S_1^{\ddagger} = -27.5 \pm 3.4$; for $[Co(bmen)_2CO_3]^+$, $k_0 = 1.33 \times 10^{-6}$ s^{-1}, $\Delta H_0^{\ddagger} = 4.6$, $\Delta S_0^{\ddagger} = -66$; $k_1 = 5.54 \times 10^{-6}$ M^{-1} s^{-1}, $\Delta H_1^{\ddagger} = 28.3$, $\Delta S_1^{\ddagger} = 12.2$. The tme system shows a deuterium isotope effect with $k_1^D/k_1^H = 2.2$, consistent with a rapid pre-equilibrium protonation followed by rate controlling ring opening. The variations of k_1 with the amine ligand are in the order $(en)_2 \approx (pn)_2 > (tme)_2 \gg (bmen)_2$. Since the latter two systems have almost the same electron donor ability, based on their pK_a values, their large reactivity difference must be ascribed to steric effects of the $-N(CH_3)$ groups in bmen. The data from a large number of previous studies of such carbonate chelate ring openings have been reanalysed, and the reactivity patterns are discussed.

Key words: Kinetics and mechanism; Steric effect; Cobalt complexes; Diamine complexes; Carbonato complexes; Decarboxylation; Aquation

Introduction[**]

The zinc(II) enzyme carbonic anhydrase allows the $CO_2 + H_2O \rightleftharpoons HCO_3^-$ equilibrium to be rapidly maintained, and the mechanism of the biological system has been the subject of numerous studies [1]. Since a zinc(II) carbonate or bicarbonate complex is considered to be involved in the enzymic reaction, there has been considerable interest in the kinetics of carboxylation and decarboxylation of metal complexes and this subject has been extensively reviewed recently by Palmer and van Eldik [2]. Kinetic studies have been done on an especially wide range of carbonatotetraamine–cobalt(III) complexes of the general formula $[(N)_4CoCO_3]^+$, where $(N)_4$ refers to any combination of uni-, bi- tri- or tetradentate amine ligands. There are some studies on analogous chromium(III) and rhodium(III) systems [3, 4].

In acidic solution, the decarboxylation of the $[(N)_4CoCO_3]^+$ complexes typically has a pseudo-first-order rate constant given by eqn. (1) for $[H_3O^+] \gg$ [cobalt(III)]. It has been shown, for $(N)_4 = (NH_3)_4$

$$k_{obs} = k_0 + k_1[H_3O^+] \qquad (1)$$

---

[*] Author to whom correspondence should be addressed.

[†] Present address: Department of Chemistry, Faculty of Science, Kuwait University, PO Box 5969, Safat 13060, Kuwait.

[**] Ligand abbreviations used in this study: en = ethylenediamine; pn = propylenediamine; bmen = *N,N'*-dimethyl-1,2-diaminoethane; tme = 2,3-dimethyl-2,3-diaminobutane; tn = trimethylenediamine; py = pyridine; bpy = bipyridine, phen = 1,10-phenanthroline; tren = 2,2',2''-triaminotriethylamine; trpn = 3,3',3''-triaminotripropylamine; trien = triethylenetetraamine; Me_2trien = 3(*S*), 8(*S*)-dimethyltriethylenetetraamine; dmtr = 4,7-dimethyltriethylenetetraamine; cyclam = [14]aneN_4 = 1,4,8,11-tetraazacyclotetradecane; cyclen = [12]aneN_4 = 1,4,7,10-tetraazacyclododecane; Me_2[14]dienN_4 = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; Me_6[14]dieneN_4 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; 3,2,3-tet = 4,7-diazadecane-1,10-diamine; 2,3,2-tet = 3,7-diazanonane-1,9-diamine; edda = ethylenediaminediacetate; nta = nitrilotriacetate.

SSDI 0020-1693(94)03957-P

[5], $(en)_2$, $(phen)_2$ and $(bipy)_2$ [6], that the acid catalysed reaction proceeds with initial breaking of the Co–O bond followed by breaking of the C–O bond to yield CO_2. It is generally assumed [7], consistent with deuterium isotope effects [8, 9], that a rapid pre-equilibrium protonation precedes the ring opening for the k_1 path. The reaction sequence for the uncatalysed path (k_0) is not known but is generally assumed to involve nucleophilic attack of water on either the carbonate carbon or the Co(III), followed by a combination of proton transfers and chelate ring opening. Studies on a number of monodentate carbonato complexes indicate that their decarboxylation is fast compared to the chelate ring opening for most systems so that the latter is the rate controlling step. The reaction sequence is summarised in Scheme 1. If $K_a \gg [H^+]$, then Scheme 1 leads to the expression for k_{obs} given by eqn. (1), with $k_1 = k_1'/K_a$. The variations in k_1 with $(N)_4$ may be due to changes in either k_1' or K_a, while variations in k_0 may reflect the susceptibility of the system to nucleophilic attack or the ease of breaking the Co–O bond.

$$(\mathrm{N})_4\mathrm{Co(CO_3)^+ + H_3O^+} \overset{K_a}{\rightleftharpoons} (\mathrm{N})_4\mathrm{Co(CO_3H)^{2+} + H_2O}$$

$$(\mathrm{N})_4\mathrm{Co(CO_3)^+ + H_2O} \xrightarrow{k_0} (\mathrm{N})_4\mathrm{Co(OH_2)(CO_3)^+}$$

$$(\mathrm{N})_4\mathrm{Co(CO_3H)^{2+} + H_2O} \xrightarrow{k_1'} (\mathrm{N})_4\mathrm{Co(OH_2)(CO_3H)^{2+}}$$

$$(\mathrm{N})_4\mathrm{Co(OH_2)(CO_3H)^{2+}} \xrightarrow{\text{fast}} (\mathrm{N})_4\mathrm{Co(OH_2)(OH)^{2+} + CO_2}$$

$$(\mathrm{N})_4\mathrm{Co(OH_2)(CO_3)^+ + H_3O^+} \xrightarrow{\text{fast}} (\mathrm{N})_4\mathrm{Co(OH_2)(OH)^{2+} + CO_2 + H_2O}$$

Scheme 1.

Studies in which the $(N)_4$ ligands were varied have shown variations of 10^6 in k_1 and these changes have been attributed to the geometric arrangement of the ligands [10, 11], steric hindrance [10, 12, 13], ligand unsaturation [8, 11, 14] and ligand basicity [5, 10]. The values of k_0 vary by about 10^4 for the same range of $(N)_4$ ligands. The present study explores the steric effects of the $(N)_4$ ligands by comparing the 1,1,2,2-tetramethylethylenediamine (tme) and *N,N'*-dimethylethylenediamine (bmen) systems in which $-CH_3$ substituents are introduced on the ethylene backbone and the coordinating nitrogens, respectively.

Experimental

Materials

1,1,2,2-Tetramethylethylenediamine (tme) was prepared by $SnCl_2/HCl$ reduction of 2,3-dinitro-2,3-dimethylbutane (Aldrich Chemical Co.) and purified by distillation at reduced pressure as described previously [15]. *N,N'*-Dimethylethylenediamine (bmen) was used as obtained from Fluka Chemical Co. Other standard chemicals were of reagent grade and deionised; doubly distilled water was used throughout.

$[Co(tme)_2CO_3]ClO_4 \cdot H_2O$ was prepared as described previously [16] and recrystallised from hot water. *Anal.* Calc. for $C_{13}H_{32}N_4O_7ClCoH_2O$: C, 33.31 H, 7.31; N, 11.95. Found: C, 33.12; H, 7.25; N, 12.16%.

$[Co(bmen)_2CO_3]ClO_4$ was prepared essentially as described previously for $[Co(tn)_2CO_3]ClO_4$ [17] by the reaction of $Na_3[Co(CO_3)_3] \cdot 3H_2O$ and two equivalents of bmen. The product was recrystallised twice from hot ethanol and obtained in only 5% yield. No attempt was made to optimise the yield. *Anal.* Calc. for $C_9H_{24}N_4O_7ClCo$: C, 27.39; H, 6.13; N, 14.2. Found: C, 27.08; H, 6.01; N, 14.18%.

Kinetic measurements

The kinetic runs were initiated by dissolving a weighed amount of the carbonato complex in 1.0 M $NaClO_4$ and adding an equal volume of an $HClO_4/NaClO_4$ solution at the appropriate concentration. Both solutions were equilibrated at the desired temperature before mixing. The reaction solution was transferred to a thermostatted 2.0 cm path length cell in the spectrophotometer. The initial concentrations of $[Co(tme)_2CO_3]^+$ and $[Co(bmen)_2CO_3]^+$ ions were 2.5 and 1.0 mM, respectively.

The kinetic observations were made or recorded on a Hewlett-Packard 8451 diode array spectrophotometer equipped with a temperature controlled metal cell holder maintained at the desired temperature (±0.1°C) by water circulating through the cell holder. The reaction was monitored at 366 and 520 nm for $[Co(tme)_2CO_3]^+$ and 528 nm for $[Co(bme)_2CO_3]^+$. The absorbance–time data was analysed by non-linear least-squares to obtain the k_{obs} values for each run. Errors quoted are one standard deviation for linear fits of the $[H_3O^+]$ dependence and 95% confidence limits for the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ parameters.

The reaction of $[Co(tme)_2CO_3]^+$ in D_2O were done in the manner just described with 99.8% D_2O (General Intermediates of Canada) as the solvent. Corrections were applied for the 2 to 8% H_2O introduced with the $HClO_4$.

Results and discussion

The electronic spectral properties of the reactant and product complexes are summarised in Table 1. During the aquation of $[Co(tme)_2CO_3]^+$ two isosbestic points are observed at 431 and 476 nm and the final

TABLE 1. Electronic spectra of the Co(III) complexes studied

Complex ion	Medium	λ_{max} (ϵ)[a]	λ_{max} (ϵ)[a]
$[Co(tme)_2CO_3]^+$ [b]	1.0 M $NaClO_4$	520 (144)	366 (146)
cis-$[Co(tme)_2(OH_2)_2]^{3+}$	0.1 M $HClO_4$	510 (100)	368 (90)
$[Co(bmen)_2CO_3]^+$	1.0 M $NaClO_4$	528 (134)	370 (120)
cis-$[(bmen)_2(OH_2)_2]^{3+}$ [c]	0.15 M $HClO_4$	530 (97)	370 (95)
trans-$[Co(bmen)_2(OH_2)_2]^{3+}$ [d]	0.15 M $HClO_4$	520 (29)	367 (38)

[a] λ_{max} in nm and ϵ in M^{-1} cm^{-1}. [b] Data given in ref. 16. [c] Measured after 4 half-times for aquation at 63 °C of $[Co(bmen)_2CO_3]^+$. [d] Measured after keeping the *cis*-isomer for 10 h at 75 °C.

TABLE 2. The observed and calculated pseudo-first-order rate constants (s^{-1}) for the aquation of $[Co(N_2)_2CO_3]^+$ complexes in 1.00 M $HClO_4/NaClO_4$

(N_2)	Temp. (°C)	$[H_3O^+]$ (M)	$10^3\times k_{obs}$	$10^3\times k_{calc}$
tme	20.0	0.010	0.37	0.37
tme	20.0	0.025	0.65	0.67
tme	20.0	0.050	1.15	1.18
tme	20.0	0.075	1.82	1.68
tme	20.0	0.100	2.28	2.19
tme	20.0	0.150	3.19	3.20
tme	20.0	0.200	3.97	4.21
tme	25.0	0.010	0.49	0.49
tme	25.0	0.025	0.90	0.93
tme	25.0	0.050	1.69	1.65
tme	25.0	0.075	2.36	2.37
tme	25.0	0.100	3.26	3.09
tme	25.0	0.125	3.87	3.81
tme	25.0	0.150	4.56	4.53
tme	25.0	0.175	5.11	5.25
tme	25.0	0.200	5.76	5.98
tme	30.0	0.010	1.01	0.95
tme	30.0	0.025	1.42	1.54
tme	30.0	0.050	2.50	2.52
tme	30.0	0.075	3.54	3.50
tme	30.0	0.100	4.33	4.48
tme	30.0	0.125	5.82	5.46
tme	35.0	0.010	1.25	1.25
tme	35.0	0.025	2.09	2.08
tme	35.0	0.050	3.86	3.46
tme	35.0	0.075	4.85	4.84
tme	35.0	0.100	6.08	6.22
bmen	55.0	0.150	0.104	0.101
bmen	55.0	0.300	0.158	0.173
bmen	55.0	0.400	0.235	0.220
bmen	55.0	0.550	0.296	0.292
bmen	63.0	0.150	0.240	0.241
bmen	63.0	0.300	0.460	0.446
bmen	63.0	0.400	0.564	0.583
bmen	63.0	0.550	0.796	0.788

spectrum is stable and consistent with *cis*-$[Co(tme)_2(OH)_2]^{3+}$. For $[Co(bmen)_2CO_3]^+$, there are four isosbestic points at 347, 426, 466 and 601 nm, and the product spectrum of *cis*-$[Co(bmen)_2(OH_2)_2]^{3+}$ changes over a period of 10 h at 75 °C to that of *trans*-$[Co(bmen)_2(OH_2)_2]^{3+}$.

The variations of k_{obs} with $[H_3O^+]$ and temperature for $[Co(tme)_2CO_3]^+$ and $[Co(bmen)_2CO_3]^+$ are given in Table 2 and a typical plot is illustrated in Fig. 1 for the former system. The dependence of k_{obs} on $[H_3O^+]$ is consistent with eqn. (1) for both complexes as can be seen from a comparison of the observed and calculated least-squares best fit values in Table 2. The values of k_0 and k_1 at different temperatures and the activation parameters are summarized in Table 3. The k_0 for $[Co(bmen)_2CO_3]^+$ is too small to be properly defined by the experiments.

The deuterium isotope effect on the aquation of $[Co(tme)_2CO_3]^+$ was determined at 25 °C for $[HClO_4]$ between 0.020 and 0.075 M with solutions containing 98 to 92% D_2O, depending on the $HClO_4$ concentration. The results have been analysed and corrected for the variation in D_2O content using eqn. (2)

$$k_{obs}=(k_0{}^H+k_1{}^H[H_3O^+])]f_{H_2O} + (k_0{}^D+k_1{}^D[D_3O^+])f_{D_2O} \qquad (2)$$

where f_{H_2O} and f_{D_2O} are the mole fractions of H_2O and D_2O in the medium, $k_0{}^H$ and $k_1{}^H$ are rate constants in H_2O and $k_0{}^D$ and $k_1{}^D$ are corresponding values in D_2O. Since the former rate constants and the mole fractions are known, the rate constants in D_2O can be calculated from eqn. (2). The results give $k_0{}^D=(3.1\pm1.5)\times10^{-4}$ s^{-1} and $k_1{}^D=(6.3\pm0.5)\times10^{-2}$ M^{-1} s^{-1}. Then the isotope effects for aquation of $[Co(tme)_2CO_3]^+$ are $k_0{}^D/k_0{}^H=1.5$ and $k_1{}^D/k_1{}^H=2.2$ The larger effect for the k_1 path is consistent with the protonation equilibrium in Scheme 1 as discussed previously by Harris and Hyde [8] and Hay and Jeragh [9].

The $(bmen)_2$ system is remarkable in having the smallest k_1 at 25 °C and the largest $\Delta H_1{}^{\neq}$ thusfar observed for the ring opening of $(N)_4Co^{III}CO_3$ complexes. The extreme position is especially noteworthy if attention is confined to aliphatic amine ligands for which the next most reactive system, β-Me_2trien, has a rate constant 10^2 times larger than $(bmen)_2$. The most obvious explanation for this low reactivity would seem to be a steric effect of the -$N(CH_3)$ groups on

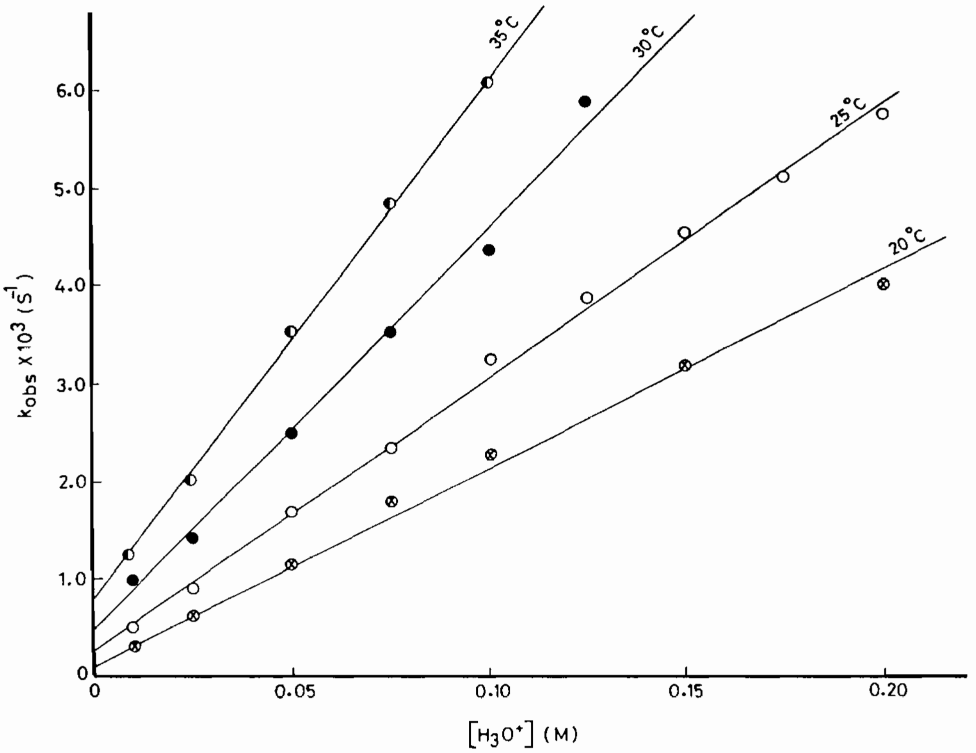

Fig. 1. Variation of k_{obs} with [H_3O^+] for the hydrolysis of [$Co(tme)_2CO_3$]$^+$ in aqueous perchloric acid at different temperatures [$\mu = 1.0$ M ($NaClO_4$]: ⊗, 20; ○, 25; ●, 30; ◐, 35 °C.

TABLE 3. Rate constants and activation parameters for the aquation of [$Co(N_2)_2CO_3$]$^+$ complexes in 1.00 M $HClO_4/NaClO_4$

(N_2)	Temp. (°C)	$10^4 \times k_0$[a] (s^{-1})	$10^2 \times k_1$ (M^{-1} s^{-1})
tme	20.0	1.66 ± 0.13	2.02 ± 0.04
	25.0	2.04 ± 0.11 (2.58)[b]	2.89 ± 0.03 (2.86)[b]
	30.0	5.62 ± 0.45	3.92 ± 0.13
	35.0	7.01 ± 0.21	5.51 ± 0.07
$\Delta H^{\neq}$ [c] (kcal mol^{-1})		18.6 ± 0.18	11.35 ± 0.095
$\Delta S^{\neq}$ [c] (cal mol^{-1} K^{-1})		−12.6 ± 8.6	−27.5 ± 3.4
bmen	55.0	0.30 ± 0.15	0.48 ± 0.05
	63.0	0.36 ± 0.14	1.37 ± 0.05
	25.0	(0.014)[b]	(0.00055)[b]
$\Delta H^{\neq}$ [c] (kcal mol^{-1})		4.5 ± 10	28.3 ± 0.36
$\Delta S^{\neq}$ [c] (cal mol^{-1} K^{-1})		−66 ± 215	12.2 ± 21

[a] Rate constants determined from [H_3O^+] dependence at each temperature; errors limits are one standard deviation. [b] Values calculated from the activation parameters. [c] Determined from a non-linear least-squares fit of all the k_{obs} values; errors are 95% confidence limits.

the bmen ligand. This manifest itself as a $\Delta H_1^{\neq}$ which is about 14 kcal mol^{-1} higher than that for $(NH_3)_4$ or $(en)_2$, and this is only partly offset by the 24 cal mol^{-1} K^{-1} more favourable $\Delta S_1^{\neq}$. Francis and Jordan [6] suggested that the electron donor strength of the amine, as judged by its average pK_a, is related to the decarboxylation rate. But this will not explain the low reactivity of the $(bmen)_2$ complex because its average pK_a (8.7) is almost the same as that of en (8.6), and not greatly different from that of pn (8.5) and tme (8.2). Since $k_1 = k_1'/K_a$, the difference in activation parameters could be associated with either or both k_1' and K_a. If the ring opening process is a D or I_d process, then one might expect steric crowding by the amine to increase k_1'. Since the carbonyl oxygen of the chelated carbonate is rather unencumbered by the methyl groups from the bmen, it would seem that any effect on K_a would imply that protonation is required at one of the coordinated oxygens of the carbonate. The effect here could be dramatic because the methyl groups would make this

TABLE 4. Kinetic data for the carbonate chelate ring-opening in $LCo^{III}CO_3$ complexes

No.	L	μ[a] (M)	k_0[b] (s^{-1})	$\Delta H_0^{\neq}$ (kcal mol^{-1})	$\Delta S_0^{\neq}$ (cal mol^{-1} K^{-1})	k_1 (M^{-1} s^{-1})	$\Delta H_1^{\neq}$ (kcal mol^{-1})	$\Delta S_1^{\neq}$ (cal mol^{-1} K^{-1})	Ref.[c]
1	$(NH_3)_4$	0.5	(1.3×10^{-4})			1.5	13.7 ± 4	-11.5 ± 13	19*
2	$(en)_2$	0.5	1.2×10^{-4}	18 ± 3	-15 ± 9	0.6	13.8 ± 1	-13 ± 3	10
3	*cis*-$en(H_2O)_2$	1.0	9.3×10^{-2}	22.7 ± 7	8.4 ± 24	0.26	13.7 ± 2	-15 ± 7	20*
4	$(pn)_2$	0.1–0.3	1.0×10^{-4}	18 ± 3	-15 ± 9	0.5	14 ± 3	-13 ± 9	20
5	$(tn)_2$	0.1–0.3	0.8×10^{-4}	16 ± 3	-21 ± 9	0.8	12 ± 3	-19 ± 9	20
6	tren	0.5	(1.7×10^{-4})			2.2	15.2 ± 2	-6.0 ± 4	10*
7	trpn	1.0	1.7×10^{-4}	13.7 ± 5	-30 ± 18	1.0×10^{-2}	14.7 ± 2	-18 ± 5	unpub[d]
8	*β*-(2,3,2-tet)	0.5	(1.0×10^{-4})			0.17	9.3 ± 2	-31 ± 6	12*
9	*β*-(3,2,3-tet)	0.5	(4.0×10^{-5})			2.6×10^{-2}	18.2 ± 1	-4.9 ± 4	12*
10	$(tme)_2$	1.0	2.6×10^{-4}	18.6 ± 0.2	-12.6 ± 8.6	2.9×10^{-2}	11.4 ± 0.1	-27.5 ± 3	this work
11	$(bmen)_2$	1.0	(1.4×10^{-6})			5.5×10^{-6}	28.3 ± 0.4	12.2 ± 21	this work
12	*cis*-$en(NH_3)_2$	0.50	(3.0×10^{-5})			0.94	16.7 ± 0.8	-2.6 ± 3	10*
13	*trans*-$en(NH_3)_2$	0.5	(1.1×10^{-4})			8.8	9.9 ± 1	-21 ± 4	10*
14	*α*-trien	0.5	(1.5×10^{-4})			5.7	16.2 ± 2	-0.6 ± 7	10*
15	*β*-trien	0.5	(1.0×10^{-5})			0.19	16.5 ± 2	-6.5 ± 8	10*
16	*α*-Me_2trien	1.01	$(\sim3\times10^{-4})$			2.1×10^{-2}	19.7 ± 0.6	0.02 ± 2	11, 21*
17	*β*-Me_2trien	1.0	(5.5×10^{-4})			6.2×10^{-4}	19.3 ± 0.5	-8.5 ± 2	11, 21*
18	cyclam	0.5				1.3×10^{-3}	20.6 ± 0.4	-2.6 ± 1.3	13
19	cyclen	0.5				7.9 ± 10^{-3}	21.0 ± 2	2.3 ± 5	22*
20	$Me_2[14]dieneN_4$	0.5	(7.5×10^{-5})			1.5×10^{-2}	19.8 ± 1	-0.30 ± 3	9*
21	$Me_6[14]dieneN_4$	0.25				1.0×10^{-2}	24.2 ± 1	13 ± 2	14*
22	$(byp)_2$	1.0				2.2×10^{-4}	22.3 ± 2	-1.5 ± 5	6
23	$(phen)_2$	1.0				1.5×10^{-4}	20.4 ± 2	-8.6 ± 5	6
24	$(py)_4$	1&5	(1.3×10^{-6})			6.5×10^{-6}	26.7 ± 1	-7.4 ± 4	23*
25	*cis*-$py_2(H_2O)_2$	1.0	7.5×10^{-5}	26.5 ± 9	8.5 ± 29	3.1×10^{-4}	20.9 ± 5	-4.6 ± 14	24*
26	$py_3(H_2O)$	1.0				4×10^{-4}			18, 24
27	$py_2(CO_3)$	0.5	8.7×10^{-5}	21.9 ± 5	-3.6 ± 17	7.9	16.8 ± 5	1.9 ± 15	25*
28	*α*-(edda)	2.0	(1×10^{-4})			1.2×10^{2}	13.6 ± 3	-3.4 ± 9	26*
		1.0	2.1×10^{-3}	21.9 ± 6	2.8 ± 19	79	15.8 ± 2	3.1 ± 7	27*
29	*β*-(edda)	2.0	4.7×10^{-4}	8.7 ± 10	-44 ± 32	2.8	13.4 ± 3	-11.4 ± 9	26*
		1.0	3.6×10^{-4}	23.1 ± 9	3.0 ± 31	3.0	16.6 ± 3	-0.7 ± 8	27*
30	(nta)	2.0	(3.0×10^{-3})			45	16.0 ± 2	2.8 ± 7	28*

[a] Ionic strength for the study. [b] Values in brackets are assessed, on the basis of reanalysis, to be too uncertain to permit calculation of activation parameters; the value of k_0 is that given by the original authors. [c] Systems designated by * have been reanalysed as described in the text (see footnote below). [d] S.S. Massoud and R.B. Jordan, results to be published along with the carboxylation reaction.

site hydrophobic and decrease the solvation of the protonated species. One problem with assigning the slowness of the $(bmen)_2$ system to a K_a effect is that Laier *et al.* [18] have estimated, for the similarly unreactive $(py)_4CoCO_3^+$ complex, that $K_a\approx0.4$ M for $(py)_4CoCO_3H^{2+}$. Then other systems which are 10^4 to 10^6 times more reactive would need to have K_a in the 10^{-5} M range, but this is inconsistent with the assumption that $K_a \gg [H^+]$ in deriving the rate law for these systems. It is possible that the K_a measured by Laier *et al.* refers to protonation of the carbonyl oxygen while protonation of a Co–O oxygen is required for ring opening.

There have been a number of discussions of other factors that appear to affect the decarboxylation rate of $(L)_4Co^{III}CO_3$ systems. Any analysis which focuses on the rate constants is subject to a fundamental difficulty in this area because the $\Delta H^{\neq}$ values cover a wide range so that rate constant arguments are dependent on the temperature used (usually 25 °C). Palmer and van Eldik have noted that the $\Delta H_1^{\neq}$ and $\Delta S_1^{\neq}$ values show a very rough isokinetic correlation, while the correlation for $\Delta H_0^{\neq}$ and $\Delta S_0^{\neq}$ is very good. In order to examine these activation parameters more closely, we have reanalysed* the available published kinetic data and the results along with other data are given in Table 4. One conclusion from this analysis is that some of the pub-

---

*This analysis involved fitting the $[H^+]$ or pH dependence at each temperature to assess the validity of the k_0, based on a comparison of the k_0 value and its 95% confidence limit. Then the complete data set of $[H^+]$ or pH and temperature were fitted by non-linear least-squares to determine the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values. Each rate constant was weighted by its reciprocal so that they have equal influence on the fit. For some systems in which a leveling effect is observed at high acidity data for $pH \geqslant 1$ were used, and a lower pH limit of 4 was used to avoid possible complications from the reverse reaction.

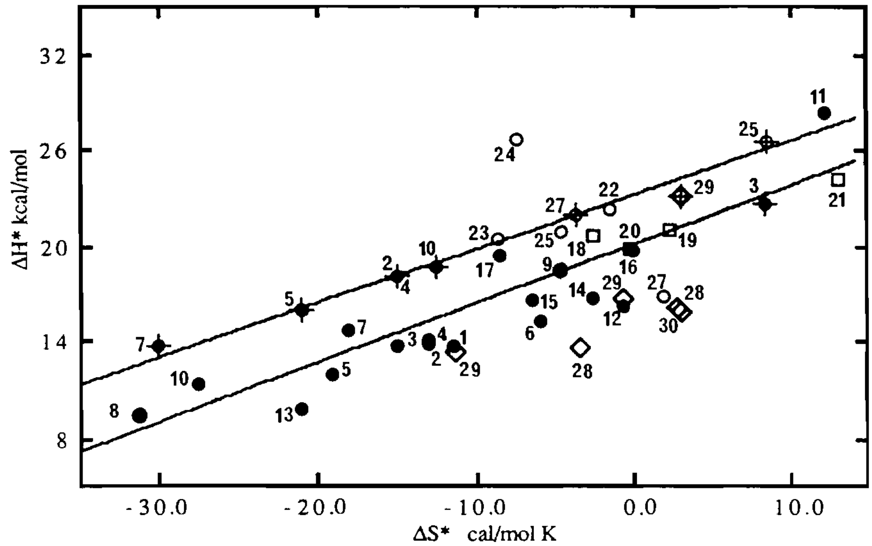

Fig. 2. Isokinetic plots for k_0 and k_1 for the carbonate ring opening of $(L)_4CoCO_3^+$ complexes. Values for k_0 are distinguished by a (+) through the point. The symbols refer to aliphatic amines (●), aromatic amines (○), cyclic amines (□) and aminocarboxylates (◇). The lines are eye guides only. For numbering of the complexes refer to Table 4.

lished k_0 values and activation parameters are less certain than appears from the published numbers. The isokinetic relationship for the remaining k_0 parameters is maintained (Fig. 2), but may be in part a fortuitous result of the fact that most of the rate constants are of the order of 10^{-4} s^{-1} at 25 °C. The revised data give a somewhat better isokinetic relationship for $\Delta H_1^{\neq}$ and $\Delta S_1^{\neq}$ (Fig. 2)* than that found by Palmer and van Eldik [2].

Systems in which an amine chelate ring bridges the positions *trans* to the carbonate ligand are generally more reactive than the structural isomer without this feature. Thus α-trien and α-Me$_2$trien [3] have k_1 at 25 °C 30 times larger than the corresponding β isomer and the effect is almost entirely due to a 6 to 10 cal mol^{-1} K^{-1} more favourable $\Delta S^{\neq}$. The α- and β-edda systems have a similar reactivity difference also mainly due to a more favourable $\Delta S^{\neq}$ for the α isomer. However, this $\Delta S^{\neq}$ effect is not maintained for the *trans*- and *cis*-en(NH$_3$)$_2$ systems where the *trans* isomer has a 9.4 times larger k_1 due to a 7 kcal mol^{-1} more favourable $\Delta H^{\neq}$ which is compensated by an 18 cal mol^{-1} K^{-1} less favourable $\Delta S^{\neq}$. It is interesting to note that, if the *trans*- and *cis*-en(NH$_3$)$_2$ systems followed the constant $\Delta H^{\neq}$ and changing $\Delta S^{\neq}$ pattern, then *trans*-en$(NH_3)_2CoCO_3^+$ would have $k_1 \approx 45$ M^{-1} s^{-1} (25 °C), compared to the measured value of 8.8 M^{-1} s^{-1}. If this estimate is correct, then the system would be complex because the ring opening and subsequent decarboxylation ($k \approx 0.6$ s^{-1}) would be competitive for pH < 3. The kinetic effect of the chelate ring coplanar with the carbonate has been ascribed to ring strain because the N–Co–N angle *trans* to carbonate prefers to open to ~100° and this preference will be inhibited by a chelate ring subtending this position.

The effect of the amine backbone structure shows some regularities in that the addition of a CH$_2$ group causes a 1 to 2 kcal mol^{-1} K^{-1} decrease in $\Delta H_1^{\neq}$ and 6 to 12 cal mol^{-1} decrease in $\Delta S_1^{\neq}$ for en versus tn and tren versus trpn. The presence of one CH$_3$ group on C in pn has a negligible kinetic effect when compared to en, but four such groups in tme cause k_1 to decrease 30-fold because of a 14 cal mol^{-1} K^{-1} less favourable $\Delta S_1^{\neq}$, which is partly offset by a 2.5 kcal mol^{-1} more favourable $\Delta H_1^{\neq}$. The recent study of Dasgupta shows large differences in activation parameters for the β isomers of 2,3,2-tet and 3,2,3-tet. The former complex is unusual in having the lowest $\Delta H_1^{\neq}$ (9.3 kcal mol^{-1}) and most negative $\Delta S_1^{\neq}$ (−30.7 cal mol^{-1} K^{-1}) of all the aliphatic amine systems compared to more normal values of 18.2 and −4.9 for the 3,2,3-tet system. The cyclic amines are generally less reactive due to higher $\Delta H_1^{\neq}$ values in the 20 to 24 kcal mol^{-1} range for cyclam, Me$_2$[14]dieneN$_4$ and Me$_6$[14]dieneN$_4$.

The aromatic amines (py, bpy, phen) also show low reactivity again primarily because of high $\Delta H_1^{\neq}$ values. Francis and Jordan [6] suggested that this was due to poorer electron donor ability of the aromatic amines compared to the aliphatic systems and this will make K_a larger and k_1' smaller if the ring opening has dissociative character.

The aminocarboxylate systems (edda and nta) tend to have the largest k_1 values, mainly due to a more positive $\Delta S_1^{\neq}$ value. This reactivity is expected from

---

*The most obvious deviant from this plot is the $(py)_4CoCO_3^+$ system which was studied at 5 M ionic strength, and shows a very dramatic change in rate law with ionic strength.

the negative charge on these systems which would favour a smaller K_a and a larger k_1 for dissociative activation. However, the rather normal k_0 values indicate that Co–O bond breaking is not particularly favourable.

The mechanistic character of the ring opening remains unclear. If it is dissociative, then one might expect some parallel between the hydrolytic reactivity of the corresponding $(N)_4CoCl_2^+$ complex for example. However, the $(trpn)CoCl_2^+$ complex [29] is much more reactive than the other aliphatic amines, yet its carbonato complex is much less reactive than normal. As already noted, the introduction of strain through backbone methyl groups inhibits carbonato chelate ring opening in all cases, yet the opposite might be expected for a dissociative process. From all of these observations, one is left with the conclusion that the k_1 path probably involves protonation of a coordinated oxygen, and that some bond making to the entering water molecule is also involved.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support. S.S.M. thanks Alexandria University for granting a leave of absence to do this work at the University of Alberta.

References

1 D.A. Silverman and S. Lindskog, *Acc. Chem. Res., 21* (1988) 30.
2 D.A. Palmer and R. van Eldik, *Chem. Res., 83* (1983) 651.
3 D.A. Palmer, R. van Eldik, H. Kelm and G.M. Harris, *Inorg. Chem., 19* (1980) 1009.
4 J. Erikson, L. Monsted and O. Monsted, *Acta Chem. Scand., 44* (1990) 561.
5 F.A. Posey and H. Taube, *J. Am. Chem. Soc., 75* (1953) 4099.
6 D.J. Francis and R.B. Jordan, *Inorg. Chem., 11* (1972) 461.
7 T.P. Dasgupta and G.M. Harris, *J. Am. Chem. Soc., 93* (1971) 91, and refs. therein.
8 G.M. Harris and K.E. Hyde, *Inorg. Chem., 17* (1978) 1892.
9 R.W. Hay and B. Jeragh, *J. Chem. Soc., Dalton Trans.,* (1979) 1343.
10 T.P. Dasgupta and G.M. Harris, *J. Am. Chem. Soc., 93* (1971) 91.
11 D.J. Francis and G.H. Searle, *Aust. J. Chem., 27* (1974) 269.
12 F.D. Baeta, S.A. Bajue and T.P. Dasgupta, *J. Chem. Soc., Dalton Trans.,* (1990) 599.
13 T.P. Dasgupta, *Inorg. Chim. Acta, 20* (1976) 33.
14 J.A. Kernohan and J.F. Endicott, *J. Am. Chem. Soc., 91* (1969) 6977.
15 R. Sayre, *J. Am. Chem. Soc., 77* (1955) 6689.
16 R.A. Kenley, R.H. Fleming, R.M. Laine, D.S. Tse and J.S. Winterle, *Inorg. Chem., 23* (1984) 1870.
17 I.R. Jonasson, S.F. Lincoln and D.R. Stranks, *Aust. J. Chem., 23* (1970) 2267.
18 T. Laier, C.E. Schaffer and J. Springborg, *Acta Chem. Scand., Ser. A, 34* (1980) 343.
19 T.P. Dasgupta and G.M. Harris, *J. Am. Chem. Soc., 91* (1969) 3207.
20 P.M. Coddington and K.E. Hyde, *Inorg. Chem., 22* (1983) 2211.
21 R.W. Hay and B. Jeragh, *Transition Met. Chem., 5* (1980) 252.
22 R.W. Hay and B. Jeragh, *Transition Met. Chem., 4* (1979) 288.
23 K.E. Hyde, G.H. Fairchild and G.M. Harris, *Inorg. Chem., 15* (1976) 2631.
24 J.F. Glenister, K.E. Hyde and G. Davies, *Inorg. Chem., 21* (1982) 2331.
25 K.E. Hyde, E.W. Hyde, R. Baltis and G.M. Harris, *Inorg. Chem., 19* (1980) 1603.
26 R. van Eldik, T.P. Dasgupta and G.M. Harris, *Inorg. Chem., 14* (1975) 2573.
27 P.J. Garnett and D.W. Watts, *Inorg. Chim. Acta, 8* (1974) 313.
28 T.P. Dasgupta and G.M. Harris, *Inorg. Chem., 13* (1974) 1275.
29 S.S. Massoud and R.M. Milburn, *Polyhedron, 8* (1989) 275, 415.